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# EQUILIBRIUM DIAGRAM OF A VAPOR-LIQUID SYSTEM

by

J. Rünkla and E. Sürde

Transactions of the Tallin Polytechnic Institute (Tall[illegible]olutehnilise Instituudi Toimetised) Series A, No. 254, 1967.

This paper investigates certain equilibrium laws for multicomponent systems and their application to the distillation process. The equilibrium of these systems is described in special coordinates (concentration of liquid phase -- temperature -- vapor pressure and temperature -- concentration of vapor phase). The systems investigated are: 1) A binary miscible system; 2) a miscible system with saturated water vapor; 3) a binary miscible system with superheated steam.

The basis of mass transfer is the equilibrium of a system determining the distribution of the concentration between two phases. The equilibrium state is characterized by the Gibbs phase rule, determining the relation between the number of components, phases and degrees of freedom. Handbooks

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usually give the distillation process equilibrium conditions for simple systems in which the number of components is two.

This study considers certain laws for the systems mentioned above in conjunction with a study of the distillation process with water vapor, in which the number of components increases and the number of degrees of freedom changes.

For such systems the graphic representation of equilibrium conditions using two-dimensional diagrams is not sufficiently clear. A clearer representation of the equilibrium characterizing the distillation process is obtained in three-dimensional space coordinates, where a part of the space (domain) determines the number of degrees of freedom of the system and indicates the relation among the parameters of the system. The equilibrium conditions at low pressure in the presence of water vapor are also of interest, especially from the standpoint of the distribution of components between the phases.

Proceding from the above, the following systems were analyzed:

1. A binary miscible system;
2. a binary miscible system with saturated water vapor;
3. a binary miscible system with superheated steam.

The systems mentioned are represented in a three-dimensional coordinate system, where the liquid phase, temperature and saturated vapor values are laid off along the coordinate axes.

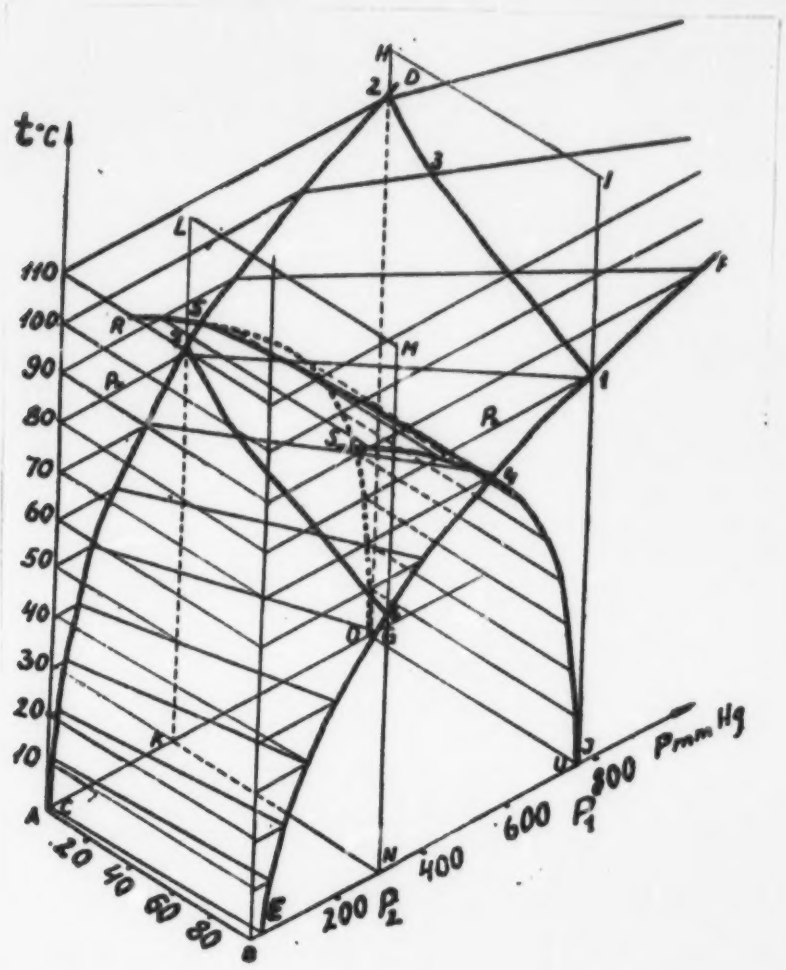


Fig. 1 Equilibrium diagram of Toluene (A) -- benzene (B) system in the coordinates: Liquid phase composition - temperature - vapor pressure (x - t - p)

## Miscible Binary System

For a system (Fig. 1) consisting of the substances A and B[1], the pressure curves CD and EF for the vapor of the pure substances, depending on the temperature, are represented graphically on the A = 100% and B = 100% planes. At an arbitrarily chosen temperature $t = t_1$, the vapor pressures of the pure substances are $P_A$, and $P_B$, respectively. The vapor pressure of the mixture at different concentrations is calculated from the formula

$$P_{AB} = \gamma_a P_A x + \gamma_b P_B (1 - x)$$

Where $P_A$ is the vapor pressure of the pure substance A,

$P_B$ is the vapor pressure of the pure substance B,

$P_{AB}$ is the total vapor pressure of the system

x is the concentration of the substance A in the liquid phase

$\gamma_a$ is the activity coefficient of substance A, and

$\gamma_b$ is the activity coefficient of substance B.

If the system obeys Raoult's law, $\gamma_a = \gamma_b = 1$, and the total vapor pressure values lie on the straight line connecting the vapor pressure values of the pure substance on the diagram, (Fig. 1). When the system does not obey Raoult's law, $\gamma_a \neq 1$ and $\gamma_b \neq 1$, and the pressure values of the pure substances $P_A$ and $P_B$ are connected by a curve.

The set of all equilibrium vapor pressure values ($P_{AB}$) under different conditions forms the curvilinear surface CDFE (Fig. 1), which we will henceforth call the equilibrium pressure surface of the systems A and B. The intersection of the equilibrium pressure surface CDFE and the total pressure

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1. Figs. 1 and 2 represent graphically the equilibrium diagrams of the toluene-benzene system.

planes $P_1$ (GHIT) and $P_2$ (KLMN) (Fig. 1) gives the curves 1 - 2 and 6 - 7. These curves characterize the changes in the boiling point of the system and the concentration when the pressure is held constant. Every arbitrarily selected intermediate point, for example 3 (Fig. 1), at the seslected total pressure $P_1$ lies on line 1 - 2 and determines uniquely the equilibrium between the liquid and vapor phase. In this case the temperature ($t_3$) and the corresponding composition of the vapor phase

$$P_1 = p_{AB} = p_A + p_B,$$
$$p_A = \gamma_a P_A x,$$
$$p_B = \gamma_b P_B (1 - x).$$

which depend on the liquid phase concentration ($x_3$) are determined.

$$y = \frac{\gamma_a P_A x}{\gamma_a P_A x + \gamma_b P_B (1 - x)},$$

where $P_A$ is the partial pressure of component A

$P_B$ is the partial pressure of component B,

y is the concentration of the component A in the vapor phase,

$P_A$ and $P_B$ are the vapor pressures of the pure substances A and B at the temperature $t_3$.

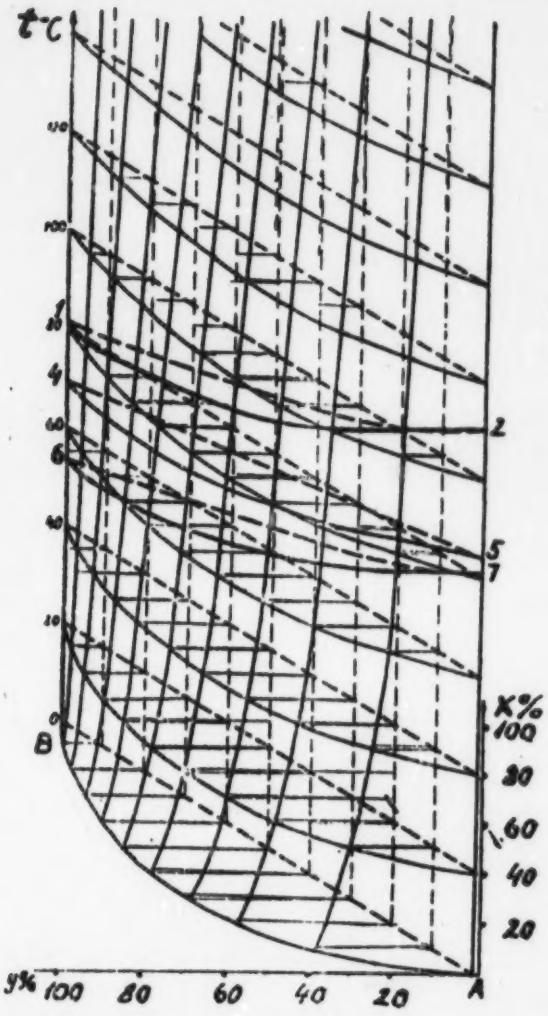


Fig. 2. Equilibrium diagram of toluene (A) - benzene (B) system in the coordinates: Temperature -- liquid phase composition -- vapor phase composition (t - x - y).

If we calculate on the basis of the proposed method the equilibrium vapor phase concentrations (y) with different liquid phase concentrations (x) at different temperatures (t) and pressures (P), we can construct, using the data obtained, a new three-dimensional diagram. The temperature (t), the liquid phase composition (x) and the vapor phase composition (y), are laid off along the axes of this diagram as shown in Fig. 2.

If we transfer the curve for the temperature change depending on the concentration (1 - 2) at the given total pressure ($P_1$) from Fig. 1 to Fig. 2, every temperature t and liquid phase concentration x determines uniquely the composition of the vapor phase (y) on the equilibrium surface. In Fig. 2 curve 1 - 2 on the equilibrium surface determines the change in the vapor phase composition (y) corresponding to the selected total pressure ($P_1$) and initial concentration (x).

The projection of the three-dimensional equilibrium curve 1 - 2 (Fig. 2) on the plane t = const can be used to calculate the statics of the process separating the system A + B at the given total pressure ($P_1$).

Binary Miscible System with Saturated Water Vapor

The substances A and B are miscible, but insoluble in water. In this case, the total pressure is determined by the sum of the vapor pressures

$$P = p_w + p_{AB}$$

where $p_w$ is the saturated water vapor pressure.

This determines the boiling point of the system for the given total pressure ($P_1$). If we plot in Fig. 1 on the diagram the difference $P_1 - p_w$ between the total pressure ($P_1$) and the water vapor pressure ($p_w$), which depends on the temperature (t), we obtain the surface ORSU. The equilibrium pressure ($p_{AB}$) surface of the distilled substances CDFE, and the surface

ORSU, formed by the difference ($P_1 - p_w$), intersect each other in Fig. 1 along the curve 4 - 5.

In Fig. 1, curve 4 - 5 shows the equilibrium state of the system of distilled substances -- the saturated water vapor at the total pressure $P_1$ at all concentrations. When the concentration (x) and temperature (t) values on curve 4 - 5 are transferred from Fig. 1 to Fig. 2, they also determine uniquely the equilibrium concentrations of the vapor phase (y). The ratio of the substances A and B in the vapor phase $\left(\frac{y_A}{y_B}\right)$ can be calculated from Fig. 2. The water vapor concentration ($y_w$) in the system is proportional to the partial water vapor pressure in the system ($p_w$). The ratio of the amount of water vapor to the amount of distilled substances in the vapor phase can be calculated on the basis of Fig. 1. It corresponds to the ratio $p_w/p - p_w$:

$$\frac{y_w}{1 - y_w} = \frac{p_w}{P - p_w}$$

where $y_w$ is the water vapor concentration in the vapor phase and $p_w$ is the partial water vapor pressure.

Binary Miscible System with Superheated Steam

During distillation with superheated steam at a total pressure $P_1$, the region in which the process can take place lies on the equilibrium pressure surface CDFE of the binary system A + B (Fig. 1), between the curve 1 - 2 (corresponding to the binary system) and the curve 4 - 5 (corresponding to the system with the saturated water vapor). The curve characterizing the actual process can have different shapes, depending on the superheated vapor pressure in the system.

The distillation can be carried out using an inert gas instead of superheated steam. Everything mentioned above will also be true for the gas. However, the surface characterizing equilibrium will not be bounded by the difference in the total pressure and the saturated water vapor pressure ($P - p_w$), as shown in Fig. 1, since curve 4 - 5, the lower bound of equilibrium surface 1 - 2 - 4 - 5, is absent due to the absence of a dew point and saturation pressure in the inert gas region y under consideration. The absence of curve 4 - 5 in Fig. 1 when an inert gas is used instead of superheated steam, follows from the Gibbs phase rule, since the absence of one liquid phase increases the number of degrees of freedom.

An analysis of different equilibrium conditions in the coordinates temperature -- liquid phase composition -- vapor phase composition (t - x - y) has shown that the vapor phase composition surface (y) is more convex at lower temperatures, (Fig. 2). At higher temperatures, the liquid phase composition surface (y) becomes less convex, and the surface may intersect with the plane $x = y$. With further increase in the temperature, the point of intersection of the surface y and the plane $x = y$ is shifted toward the center of the line $x = y$, [sic]. Physically this phenomenon characterizes the onset of an azeotropic point and its displacement with increasing temperature. The same result is also obtained in the coordinates liquid phase concentration -- temperature -- vapor pressure (x - t - P), where the onset of the azeotrope is characterized by points at which, at $t = \text{const}$,

$$P_{AB} > P_A \text{ and } P_{AB} > P_B$$

or

$$P_{AB} < P_A \text{ and } P_{AB} < P_B$$

and at P = const

$$t_{AB} < t_A \text{ and } t_{AB} < t_B$$

$$t_{AB} > t_A \text{ and } t_{AB} > t_B$$

or if the curve obtained from the intersection of the equilibrium pressure surface (CDFE in Fig. 1) with the plane P = const or t = const has an extremum. The extremum corresponds to the azeotropic point under the conditions of the system. When superheated steam is used, the conditions of the process are characterized in the coordinates: liquid phase concentration -- temperature -- vapor pressure (x - t - p) on the surface 1 - 2 - 4 - 5 by the curve drawn from the selected initial concentration and temperature to the final concentration and temperature. If $\frac{\partial t}{\partial x}$ and $\frac{\partial p}{\partial x}$ do not change sign along the entire length of the curve, the mixture can be separated in this region and no azeotrope is formed.

Three-dimensional equilibrium diagrams can be constructed on the basis of this method when the relation between the vapor pressure of the system, and the temperature and concentration is known.

Using the diagrams, equilibrium relations can be found under freely selected conditions, which can be used in the calculation of distillation processes with water vapor, and at reduced pressure.